

The Influence of Cyclic Treatments with H₂O₂ and HF Solutions on the Roughness of Silicon Surface

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The influence of cyclic treatments with H₂O₂/DIW (1:10) and HF/DIW (1:100) on the roughness of silicon surface in the wet chemical processing was investigated by atomic force microscopy (AFM). During the step of the SC-1 cleaning, there is a large increase in roughness on the silicon surface which will result in the poor gate oxide breakdown properties. The roughness of the silicon wafer after the SC-1 cleaning step was reduced by cyclic treatments of hydrogen peroxide solution and hydrofluoric acid solution instead of HF-only cleaning. AFM images after each step clearly illustrated that the average roughness of silicon surface after three times treatments with H₂O₂ and HF solutions was reduced by 10 times compared with that after the SC-1 cleaning step.

Introduction

The silicon ultra-large scale integrated circuit (ULSI) technology requires ultraclean Si surfaces which are characterized as surfaces of contaminants-free, oxides-free, micro-roughness, etc. Recently the most advanced metal oxide semiconductor (MOS) devices now require the thickness of the gate oxide as thin as 100 Å. Future giga-bit memory with a minimum feature size of 0.18 μm will need 50 Å as a thickness of the gate oxide with sufficient reliability and precise thickness uniformity. This implies that the native oxide already formed on a silicon wafer must be completely removed or the native oxide layer must be exactly uniform and thin for the future devices. Metal contamination and silicon surface roughness are considered as another two of most important parameters which can cause defect-related breakdown of gate oxides. Especially the increase of micro-roughness of the silicon surface results in the poor gate oxide breakdown properties.¹ Therefore, the microroughness on the wafer must be minimized to get the flat SiO₂/Si interface.

Wet chemical solutions are considered to be one of the most important process in Si surface cleaning.² Chemical cleaning removes oxides, carbon or metallic impurities, and reduces surface damage or roughness. After this treatment, H-terminated surface is formed which protects from contaminants between processing stages.³ Commercially 4 or 5 chemical cleaning steps are adopted to get the clean and uniform silicon surface before oxide growing process. The piranha cleaning firstly removes organic contaminants and HF solution dissolves the native oxide. The SC-1 (standard cleaning-1) and the SC-2 (standard cleaning-2) cleaning steps are following in which particles and metallic contaminants on the surface are removed. Finally pre-oxide layer formed after the SC-1 cleaning step on silicon surface is removed by dipping into HF solutions (The previous HF solution treatment may be omitted).

The traditional SC-1 cleaning step which has been proposed by W. Kern in 1970,² is still accepted in the semiconductor industry. The SC-1 solution slowly dissolves the thin native oxide layer on silicon and form a new one by oxidation of the surface. This oxide regeneration has a self-cleaning effect and aids the removal of particles by dislodging them. However, SC-1 cleaning step has some disadvantages such as metallic impurity contamination, oxide layer growth, and the increase of micro-roughness on the surface.⁴ The HF-only cleaning is, therefore, performed to decrease the roughness on silicon surface. However, the final condition of the surface is still not enough for the higher density device due to the microroughness formed after the SC-1 cleaning step. In this paper, a new method to decrease the microroughness on silicon surface after the SC-1 cleaning process is proposed. The resultant surfaces are investigated by atomic force microscopy (AFM).⁵

Experiments

The p-type 4" Si(100) wafers with intrinsic resistivity of 22.0-38.0 Ωcm were treated by sequential cleaning processes. The process started from the piranha cleaning in which wafers were dipped into the mixed solution with 1 volume of 30% H₂O₂ and 4 volumes of 98% H₂SO₄ at 120 °C for 10 minutes. Washed and dried wafers were dipped into diluted HF solution which was made of 1 volume of 49% HF and 10 volumes of deionized water (DIW). Wafers treated in two previous cleaning steps were transferred consecutively to the next step which is called SC-1 cleaning step to remove all particles. The solution used in the step was made of NH₄OH (1 volume), H₂O₂ (1 volume), and deionized water (DIW, 5 volumes). Samples were dipped into the solution for 10 minutes at 70-80 °C. Subsequent treatments were performed on washed and spin-dried wafers by dipping them into diluted H₂O₂ and HF solutions consecutively for 1 minute each. The H₂O₂ solution was diluted with deionized water by 1:10 volumetric ratio while the HF solution by 1:100. These consecutive H₂O₂ and HF

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treatments were repeated three times after SC-1 cleaning step.

The surfaces of wafers after each step were investigated by atomic force microscopy (AFM) to find how the microroughness of the surface was changed. The AFM whose model is Autoprobe CP fabricated by Park Science Instruments (PSI) was used in this experiment. The areas probed by the AFM were selected arbitrarily from the whole surface of the wafer. In addition, the total experimental procedure was repeated three times to get the general information about the change of microroughness on the surface. Figure 1 illustrates the flow chart of the experimental procedure.

Results and Discussion

The root mean square (rms) roughness data which express the distances in anstrom (\AA) from the lowest position to the highest position on silicon surface after each cleaning procedure are illustrated in Table 1. The piranha cleaning and the consecutive HF cleaning procedures do not affect the roughness on the silicon surface since they remove organic contaminants and native oxide layers, respectively. Therefore, the roughness of Si(100) surface before the SC-1 cleaning is similar to that of non-treated silicon wafer. The rms value at this point is about 1.3 \AA . However, the roughness of silicon surface increases about 10 times after the SC-1 cleaning in our experiments (see Table 1, 1.3 \AA vs 12 \AA). This abrupt increase in roughness can be explained by the oxidizing and etching treatments which occurred simultaneously in the SC-1 solution. When silicon is exposed to

Table 1. The rms roughness data of silicon surface after each cleaning step

Cleaning step	Experiment NO. (roughness, \AA)		
	1	2	3
Piranha+HF	1.5	1.3	1.4
SC-1	13	12	12
H ₂ O ₂	4.9	4.4	6.4
HF	2.5	2.3	1.9
H ₂ O ₂	2.9	2.5	2.3
HF	2.0	1.9	1.8
H ₂ O ₂	2.5	2.1	2.2
HF	1.5	1.4	1.5

the SC-1 mixture, the peroxide oxidizes the silicon surface while the NH_4OH etches this chemical oxide away.⁶ *i.e.*, a chemical oxide layer will continually be formed and dissolved as a result of the compensating effect of the two chemical components. One very important point to be mentioned is that the NH_4OH in the SC-1 cleaning step shows a relatively higher etch rate for silicon than silicon oxide.⁷ H_2O_2 , therefore, acts as an inhibitor of this silicon etching by the formation of a thin oxide layer. Recently, Aoyama *et al.*⁸ reported that chemical oxides formed on silicon surfaces during wet chemical cleaning was not uniform but had island shapes (see Figure 2). A similar situation may occur by the H_2O_2 in the SC-1 cleaning step when silicon wafers are dipped into the solution. Consequently the NH_4OH etches dominantly the Si site rather than the SiO_2 site. This unbalanced etch rate is supposed to be the reason why the roughness of silicon wafer increased abruptly after the SC-1 cleaning step in our experiments. A higher etch rate (obtained when the NH_4OH concentration is high) increases the particle removal efficiency by undercutting the particles, but causes a larger surface roughening during a 10 minute treatment. One has to find, therefore, an optimum between particle removal efficiency and silicon surface roughening. In this experiment, 1:1 ratio was used for $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ which is usually adopted. Another very important factor to increase the roughness of Si surfaces is metallic contaminants on the surface. It is impossible to be free from the metallic contamination after the SC-1 cleaning step since the solution includes metallic impurities which cannot

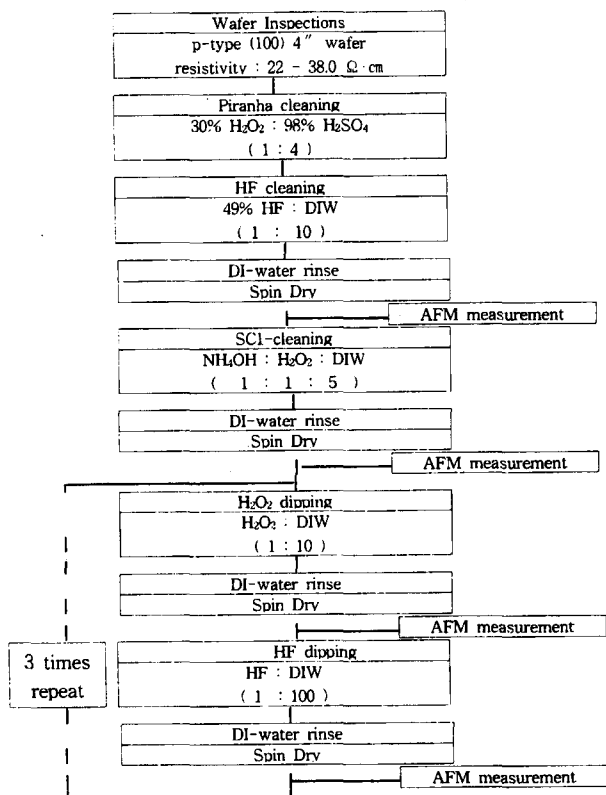


Figure 1. The flow chart of the experiment.

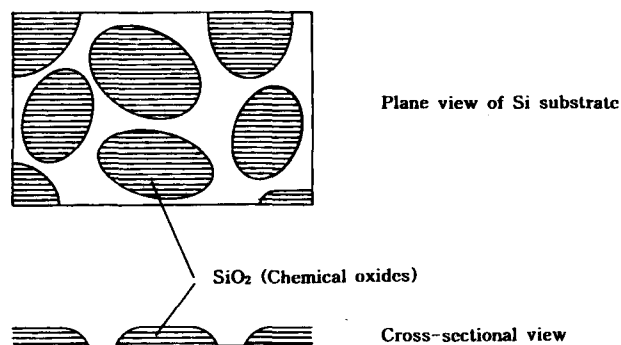


Figure 2. The island-shaped chemical oxides grown after the wet chemical cleaning.

be removed perfectly. The metal content of the chemicals and the metal contamination on the silicon wafer after the SC-1 cleaning step were reported to have linear correlation.⁴ The metallic contamination can be another reason to roughen the silicon surface after the SC-1 cleaning step. As was depicted above, especially the SC-1 cleaning step increases the roughness of the Si surface.

Treated in the H_2O_2 and HF solutions after the SC-1 cleaning step, the roughness of silicon surface decreases considerably. The rms roughness value after the one time treatment in the two solutions is 1/5 of that after the SC-1 cleaning step. The roughness decreased as the treatment of silicon wafers in the H_2O_2 and HF solutions repeats. After three times treatments the Si surface is as flat as the one after the piranha and HF treatments which is also similar to that of bare silicon wafer. The morphology change of the Si surface after each step is clearly illustrated in Figure 3. The AFM image of the silicon surface after the SC-1 cleaning step shows the shape of mountain areas as illustrated in Figure 3a, while those after the treatments in H_2O_2 and HF

solutions twice (see Figure 3b) and three times (see Figure 3c) are quite flat. These results tell us that the chemical oxide formation by the H_2O_2 is more probable not at the apex but at the valley while the oxide removal by the HF undergoes dominantly at the peak. As was mentioned above, the unbalanced etch rate by NH_4OH solution in the SC-1 cleaning step results in the roughness increase. The higher etch rate in the Si site than the SiO_2 site makes the Si site be the valley. This is the reason why the oxide formation is dominant at the valley (*i.e.*, Si site) by the H_2O_2 . The oxide removal undergoes faster at the heal because the collision between the substrate (SiO_2) and the etchant molecules are more probable at the protruded region. The diffusion of the HF molecules into SiO_2 at the heal is also faster than at the valley since the surface area of the protruded region is larger than that of the plain area. After each HF treatment, therefore, the surface roughness of silicon wafer decreases. In addition, the partial removal of adsorbed metal particles during the oxide etching also contributes the decrease of the surface roughness.

Conclusion

The roughness of silicon wafer after the SC-1 cleaning step was reduced by cyclic treatments of hydrogen peroxide solution and hydrofluoric acid solution instead of HF-only cleaning. AFM images after each step clearly illustrated that the average roughness of silicon surface after three times treatments with H_2O_2 and HF solutions was reduced by 10 times compared with that after the SC-1 cleaning step. These results tell us that the chemical oxide formation by the H_2O_2 is more probable not at the apex but at the valley while the oxide removal by the HF undergoes dominantly at the peak. The reduced roughness after the treatments with the wet chemicals may contribute to fabricate the ULSI devices. This result is consistent with the recent report⁹ that the time dependent dielectric breakdown (TDDB) of gate oxide was fairly improved when silicon wafers were treated in H_2O_2 and HF solutions.

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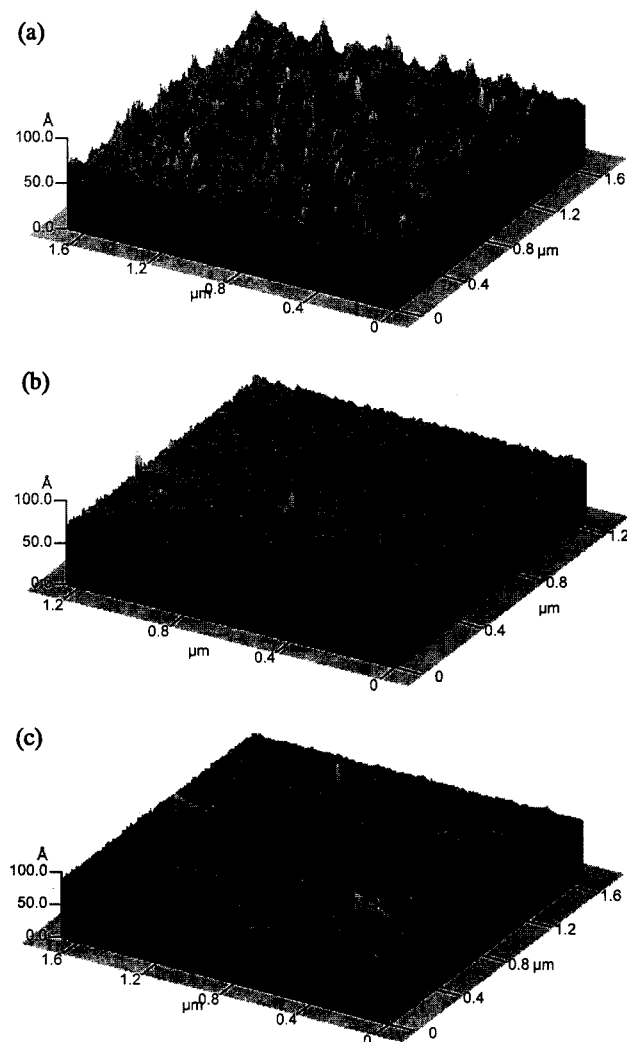


Figure 3. The AFM images of silicon surface (a) after the SC-1 cleaning, (b) after the consecutive treatment in H_2O_2 and HF solutions twice, and (c) after the consecutive treatment in H_2O_2 and HF solutions three times.

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Effect of Li on the Ionic Conductivity and Leaching in Simulated Borosilicate Glasses

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The ionic conductivity of several simulated borosilicate glasses was measured in the temperature range 150-600 °C in air. Leaching experiments were also carried out using Soxhlet apparatus at 100 °C for 7 days. As Li⁺ increased in simulated borosilicate glasses, both the ionic conductivity and leaching rate increased. The activation energy in the ionic conduction of the simulated borosilicate glasses was 1.38-1.45 eV in the high temperature region and 0.93-1.1 eV in the low temperature region.

Introduction

Electrical conductivity is one of the most important properties of glass at low temperature, especially when the glass is used as an insulating material or as a component of electrochemical devices. The electrical conductivity of glasses increases with temperature according to the exponential relation $\mu = \mu_0 \exp(-E/RT)$, where E is an activation energy for the electrical conduction. Not only the electrical conductivity (here, ionic conductivity), but also the corrosion rate is proportional to the concentration and diffusion rate of charge carriers, mostly cations in case of glass.¹ Thus, an exponential relationship between phenomena $S = \text{const} \exp(-E/RT)$ is sought, where S is the rate of attack by solvent or dissolution reaction rate and E is an activation energy, usually 15-19 kcal/mol.² In 1949, Israd and Douglas were able to obtain a quantitative correlation between the rate of removal of alkali by water attack and the electrical conductivity, where both processes involve the diffusion of sodium ions.³ However, the results of Das and Douglas showed that the correlation does not exist for less durable glasses.⁴

Borosilicate glass has been considered as one of the best matrix materials to isolate the high-level radioactive waste safely, because of its excellent chemical durability, good capability to accommodate and immobilize various radionuclides, and simple vitrification procedure, etc.⁵ In fact, a borosilicate glass such as SON68 has been produced in Marcoule in France to use in the vitrification process of high-level radioactive waste since 1978.⁵ In U.S.A., it has also been selected as the reference waste form for tank

wastes stored at Savannah River, West Valley and Hanford.⁶

In this report, the change of ionic conductivity as well as the leaching rate of simulated waste borosilicate glasses with increasing Li⁺ ion are discussed. The effect of incorporation of fission products into the borosilicate glass on ionic conductivity is also discussed.

Experimental

Synthesis. Disc-shaped samples of several simulated borosilicate glasses were prepared by a molding method. The stoichiometric amounts of SiO₂ (Merck, TLC G-type 60), B₂O₃ (Showa, C.P.), Li₂CO₃ (Aldrich, 99.997%), Na₂CO₃ (Junsei, E.P.), CaO (Fisher, ACS), Al₂O₃ (Aldrich, 99.9%), ZnO (Hayashi, C.P.), ZrO₂ (Aldrich, 99.99%), P₂O₅ (Chameleon, C.P.), Fe₂O₃ (Johnson Matthey, Spectro.), NiO (Junsei, C.P.), Cr₂O₃ (Showa, E.P.), TeO₂ (Aldrich, 99.995%), Cs₂O (Aldrich, 99% <), SrO (Aldrich, 99.995%), MoO₃ (Yoneyama, E.P.), MnO₂ (Junsei, C.P.), CoO (Junsei, C.P.), BaCO₃ (Aldrich, ACS), La₂O₃ (Wako, 99% <), CeO₂ (Aldrich, 99.999%), Nd₂O₃ (Cerac, 99.9%), Pr₆O₁₁ (Aldrich, 99.999%), CdO (Junsei, C.P.), SnO₂ (Aldrich, 99.999%), Sb₂O₃ (Shinyo, G.R.), Y₂O₃ (Aldrich, 99.999%), and Ag₂O (Kojima, 99% <) were mixed in glove box and heated in alumina crucible at 1200 °C for 2 hours (Table 1). A sample rod was made by pouring the molten glass into a preheated bright-red cylindrical mold with 12 mm diameter. The mold was made of stainless steel or Monel. It was then annealed at 500 °C for 1 hour and slowly cooled to room temperature by turning off the furnace. The cooled glass rod was cut by 1.2-1.6 mm thickness with diamond